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Concerning the volume change resulting from the sol-gel transformation of silicic acid

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CONCERNING THE VOLUME CHANGE

RESULTING FROM THE

SOL-GEL TRANSFORMATION OF SILICIC ACID

CONCERNING THE VOLUME CHANGE RESULTING FROM THE SOL-GEL TRANSFORMATION OF SILICIC ACID

A thesis presented to the Department of Chemistry of Union College, in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemistry

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Approved by Charles B Hurd

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INTRODUCTION

The subject matter of this thesis is concerned with a study of the volume change observed during the period of transition, from the sol to the gel state, of silicic acid.

Although volume change is very often a valuable clue to the mechanism of chemical and physical processes, it was until quite recently overlooked as a method of indicating the correctness of various theories of silicic acid gel formation and structure.

The first work on this problem was done by Heymann[1] in 1936. (HCl) Acid gels were used in a dilatometer to which reference will be made later. He recorded a definite volume increase throughout the apparent time of set of the gel and for an indefinite period thereafter. On the basis of these results, Heymann proposed that the formation of the gel results from the splitting out of water between simple silicic acid molecules and a subsequent polymerization to colloidal particles, the water held by chemical attraction presumably having a higher density than free water. The continued volume increase is taken to indicate that water held by the gel structure under compression is pushed out and undergoes thereby a decrease in density.

A. Riad Tourkey[2] repeated Heymann's work with some modifications, and was interested in demonstrating that the positive volume change indicated the reasonableness of the theory of fibrillar gel structure, the contraction of the proposed fibrous system being a good explanation for the volume increase during syneresis.

Curley[3] touched upon the subject of volume change in silicic acid gels in connection with his work on ester hydrolysis. After a brief treatment, he reported no volume change. This may be ascribed to two circumstances: (1) the neglect of initial readings on the ground that the temperature gradient between

dilatometer and thermostat had not yet been eliminated (to be discussed later); and (2) the dilatometer he used was quite crude, since a 3 m.m. tube was used to indicate the change and the sol itself was used as the indicator in this tube, thus almost eliminating the possibility of getting results after the gel had set.

APPARATUS

Two kinds of dilatometers were considered initially, the one used by Heymann (Fig. B) and that by Tourkey. The latter was similar to Heymann's, except that the stopcock (a) was not used, but instead was sealed off after filling. This modification was found to be impractical for use here, due to the time consumed in sealing and the danger of cracking. The Heymann dilatometer was moreover not used in its original form because it proved to be unwieldy and put a fairly high pressure of mercury on the gel. At first, therefore, a modification of this was used which employed oil in the capillary, separated from the gel by a small amount of mercury in the bottom of the tube. It was found, however, that the oil worked its way around stopcocks and past mercury so that this method was abandoned and the dilatometer shown in Figure A was used thereafter. Although there was some difficulty in preventing leakage of the sol-gel through this one remaining stopcock, with care this difficulty was overcome. The bulb had a volume of about 42 c.c., which was determined with accuracy for each run by filling from a burette. The filling was accomplished by use of a narrow funnel. The dilatometer capillary used was of .43 m.m. radius and graduations obtained by surrounding it with part of a burette, whose unit graduations were 1.05 cm. and 1.1 cm. respectively, two dilatometers being used. In later runs, the inside of the bulb was coated with

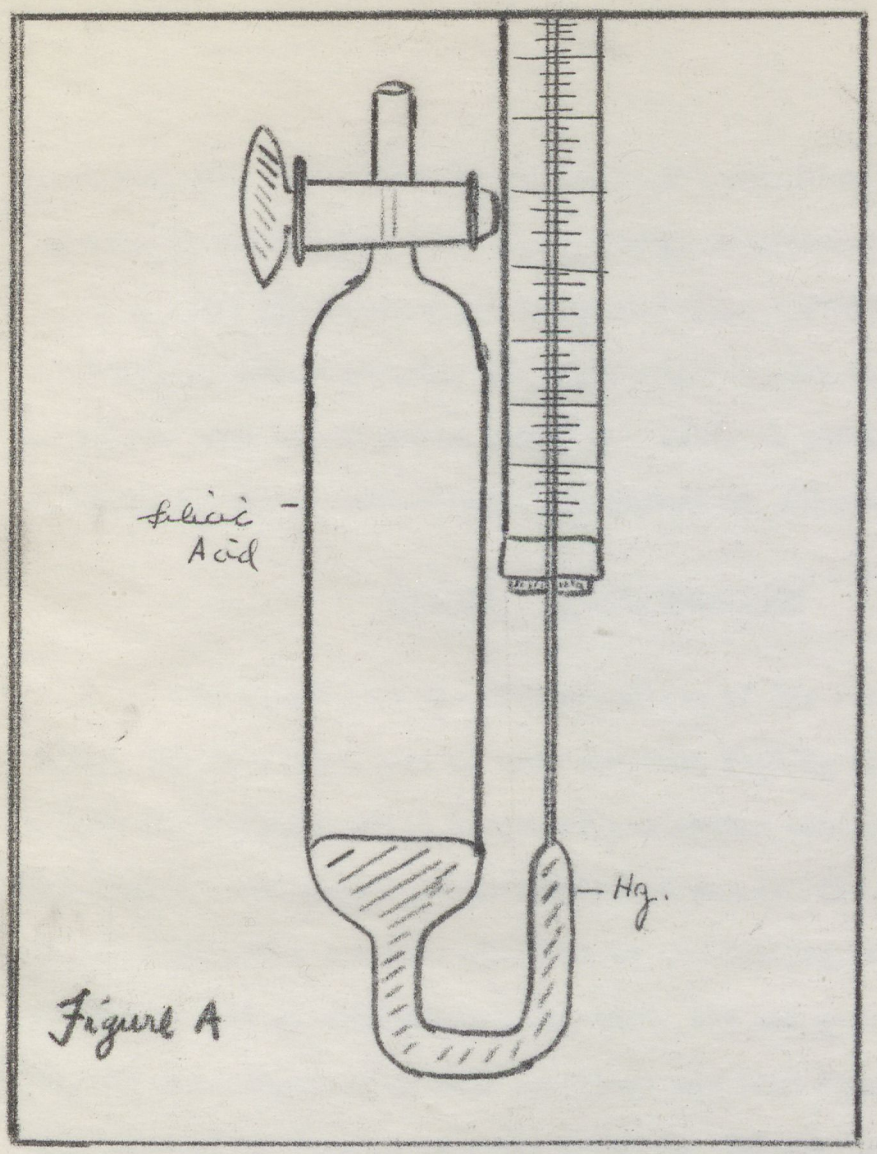


Figure A

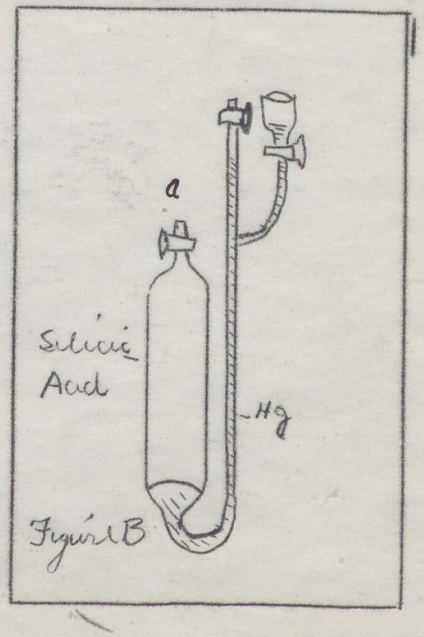


Figure B

vaseline, this being done to eliminate the gel-glass tension which would tend to nullify some of the true volume change resulting after the gel has set.

The dilatometer was thermostated in a fairly large water bath using a thyratron thermoregulator and motor stirrer, the temperature being maintained at 25° C. with an allowable error of .01°. A change of .01° corresponded to a change on the graduated capillary jacket of .02 unit.

PROCEDURE AND OBSERVATIONS

To facilitate the classification of the results obtained in this study, the sols were made up with constant Na_2SiO_3 (E Brand) content throughout (.0276 equivalents) while the water and acetic acid were varied according to the time of set desired (total volume 80 c.c.). The dilatometer used was placed in the thermostat sometime previous to the filling, which was done as follows: after the time of mixing had been noted, the sol was poured into a burette; a thistle tube terminating in a capillary was then inserted through the stopcock and the burette allowed to empty into it. The process up to this point consumed a maximum of about 3 minutes. The dilatometer was then removed from the bath momentarily and a source of air pressure applied to the stopcock opening so that the mercury could be raised to a desired point in the capillary. (By trial the correct amount of sol could be put into the stopcock tube so that no air would be present in the bulb during the run.) The dilatometer was then returned to the bath and some 7 to 10 minutes later the first reading was taken.

At this point the temperature factor is of prime importance. The temperature of the sol after mixing was found to be about 26.2° C. It may, however, be assumed that it was cooled somewhat during the filling of the dilatometer (which was itself in the 25° C. bath during filling). Therefore the first readings were

taken some 12 to 16 minutes after mixing; and indeed this time interval appeared to be justified by the results of blank runs carried out under very similar conditions. However, Heymann in his work, using sols which set within a few hours, allowed a full hour for the elimination of the sol-dilatometer temperature gradient (which may have been justifiable at a high bath temperature), thus leaving out a very considerable part of the total volume change. As a matter of fact Curley, using a bath at 32.2°, placed so much emphasis on this factor that he neglected entirely his first several readings, and concluded that there was no volume change at all.

It was early found that the positive volume change observed extended on, after the apparent setting of the gel, indefinitely. Now bearing in mind the theories of gel formation and structure proposed by other investigators, and the shape of the curves obtained by plotting time vs. volume change (Figs. 1-4, I), the following line of reasoning suggested itself to the author.

The curve mentioned above, strongly resembles the curve obtained when time is plotted against the amount of substance reacted in the course of a bi-molecular reaction. It was therefore decided to investigate the sol-gel transformation, using the hypothesis that it was of a second order reaction type, and to apply a graphic test to help determine the accuracy of such a view.

First the curves (I) were extrapolated to zero time as accurately as possible from the graphs themselves. Next, assuming the similarity of sol molecules reacting, the data on the curve was graphed according to the following equation (which refers to an ordinary second order reaction, the reacting molecules being of equal initial concentration a, and x being the amount of substance reacted in time t).

$$Kt = \frac{x}{a-x}$$

For a second order reaction this equation, plotting the t against the right hand side, must give a straight line. To apply this data, a was taken to be indicated by the total scale rise, the reading at time t was taken as x. When the data was thus plotted, a remarkably straight line was obtained except at the end, when the curve turned upwards. At this time, on conferring with Dr. Irving Langmuir, he pointed out that since the setting time as determined by the rod method could obviously not be taken as indicating the completion of the gelation process, a very slightly higher scale reading be taken as the limit and that this might be enough to straighten out the curve entirely. This suggestion was acted upon, and it was found that if the volume change for the next few hours after setting by the rod method were added to the previous total, a, that the delinquent points fell definitely into line. It was in some cases found necessary to alter slightly the result of the graphic extrapolation to obtain straight line conformity.

This result then indicated quite definitely that the gelation process of a silicic acid sol-gel system is at least very similar to a simple second order reaction, the final result being a network of primary chemical bonds. Although as previously noted, theories of second order chemical combination had been proposed earlier, this seems to be the first definite experimental evidence relating to them.

Dr. Langmuir now proposed that these results seem to corroborate his theory of silicic acid gel formations derived from consideration of viscosity changes and the energy of activation, concerning which he has not yet published anything. In brief, the theory proposes to accept the idea that gelation consists of a combination of primary silicic acid molecules with the freeing of

the scale, a change of as little as 5 or 6% of the total making possible a large change in the reaction rate constant. This type of computation may hold promise in the future of giving further insight into the mechanism of the sol-gel transformation. A wider pH range (into the basic sols) for the solutions used and a closer temperature control should give interesting results.

As might be expected, since the silica content of all the sols was constant and they were all in the acid range (silica presumably entirely reacted), the percentage volume change for all reactions was essentially constant (.05%).

Although this is a very minute effect, perhaps in the future this type of study might be elaborated to make possible a step by step study of the reaction involved with the end in view of verifying more closely the proposed theory, e.g., if it were possible to determine the volume change incident upon the mixing of the silicate with acid (first taking into account heat of reaction to avoid temperature gradient), then from the type of data given here it might be feasible to attempt a determination of the inter-molecular forces (of attraction) whose elimination produces the increase in size of the water molecules.

It was previously mentioned that the dilatometer was internally coated with vaseline in some of the later runs. This does not, however, seem to have had any appreciable effect in correcting for gel glass tension and it is assumed that the rather high elasticity of gel suffices at least for moderate volume increases in making negligible the retarding surface force, i.e., the gel not touching the glass surface may "bulge" considerably.

In conclusion it may be said that volume change, since it seems to parallel closely the actual course of the sol-gel transformation, should upon further study prove to be helpful in the critical analysis of old, and the formulation of new, theories concerning gel formation and structure.

BIBLIOGRAPHY*

1. Heymann - Trans. Faraday Soc., Vol. 32, January 1936
2. A. Riad Tourkey - Zeit. Anorg. Chemie. Band 240, 1939
3. J. B. Curley, Thesis, Union College, 1939

* Many other sources were referred to during the course of the year, and although the information obtained was very useful, it applied to the problem only incidentally, and sources have therefore not been included.

Figure 1

17 c.c. Sodium Silicate 1.6288 N
11.5 c.c. Acetic Acid 5.1750 N
51.5 c.c. Water
Temperature - 25° C. ± .01°

Dilatometer 3 - Radius .43 m.m.
Scale, 1 unit = 1.05 cm.

Volume 42.80 c.c.
Mixing time - 1:40 P.M. May 3

Table I

Scale	Time
44.00	1:56
44.20	1:58
44.40	1:59
44.60	2:02
44.80	2:08
44.95	2:13
45.05	2:17
45.15	2:20
45.25	2:26
45.35	2:33
45.40	2:38
45.50	2:45
45.55	2:51
45.60	3:00
45.70	3:14
45.78	3:25
45.85	3:39
45.90	5:51
45.96	4:05
46.08	4:40
46.14	5:00
46.18	5:45
✓46.37	9:15 P.M.
46.68	9:30 A.M. May 4

✓Apparent setting time

Table II

Time (min.)	$\frac{x}{a-x}$
22	.7
36	1.1
66	2.2
132	4.0
247	7.5
380	11.6
455	13.75

Scale limits by extrapolation:

4320–4660 ∴ .0552 moles per 1 α a = 3.40

Sample calculation:

at t = 22 min., x = 44.60–43.20 = 1.40
a–x = 2

so $\frac{x}{a-x} = \frac{1.4}{2} = .7$

Specific reaction rate $k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$

$$k = \frac{1}{22 \text{ min.}} \cdot \frac{\frac{1.4}{3.4}(.0552 \text{ moles per liter})}{.0552 \text{ m.p.l.}\left(.0552 \text{ m per liter} - \frac{1.4}{3.4}(.0552 \text{ m.p.l.})\right)}$$

$$k = .0318 \frac{\text{liters}}{\text{minutes moles}}$$

Volume change = .0237 c.c.
% change = .055%

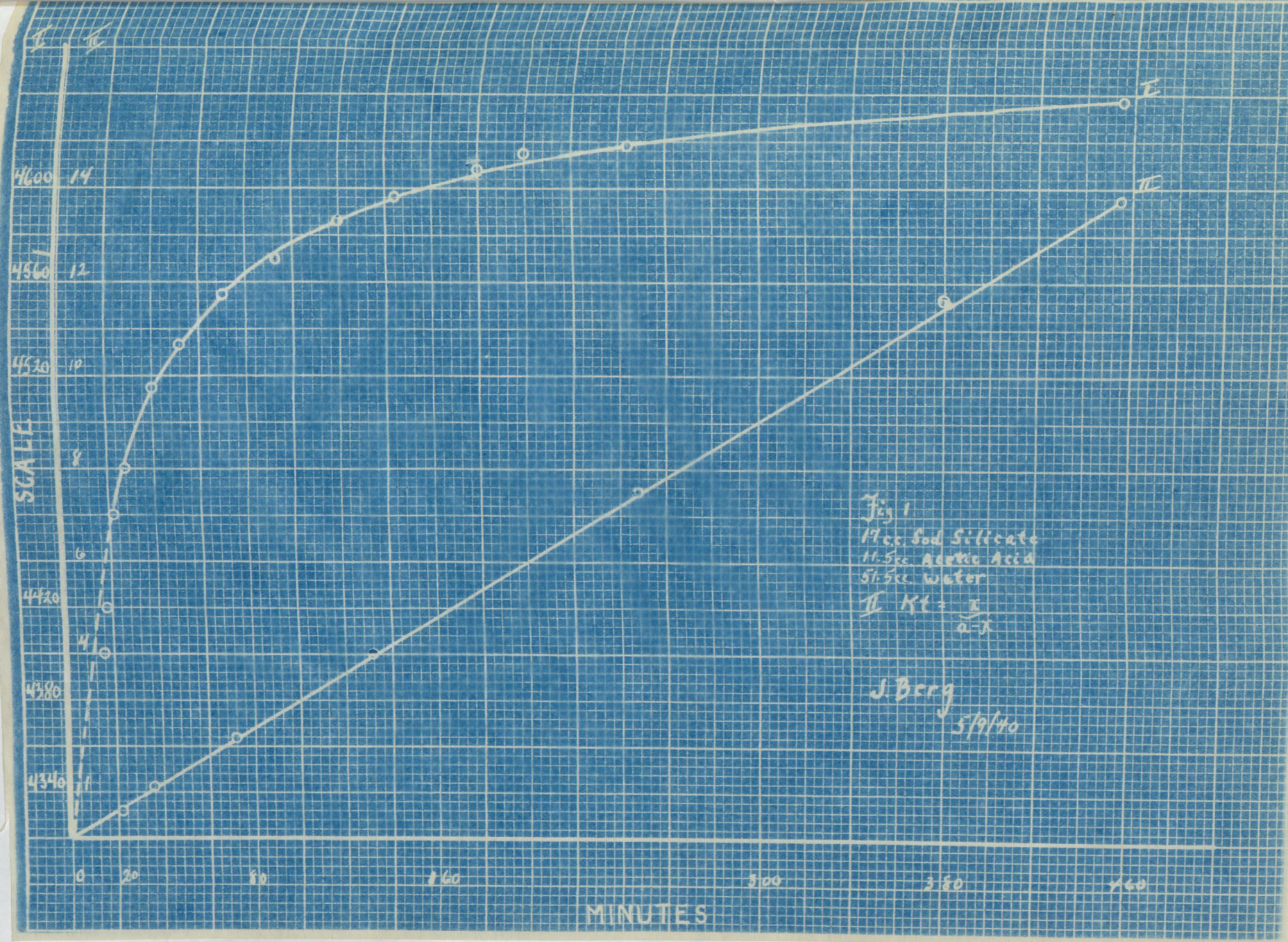

I
II
III
4600
4560
4520
4480
4440
4400
4360
4340
14
12
10
8
6
4
2
SCALE
0
30
60
120
300
360
420
MINUTES
Fig 1
17 cc Sod Silicate
11.5 cc Acetic Acid
51.5 cc Water
II Kt = x/(a-x)
J. Berg
5/9/10

Figure 2

17 c.c. Sodium Silicate 1.6268 N
8.5 c.c. Acetic Acid 5.1750 N
54.5 c.c. Water
Temperature - 25° C ± .01°

Dilatometer 3 - Radius .43 m.m.
Scale, 1 unit = 1.05 cm.
Volume 41.30 c.c.
Mixing Time - 1:19 P.M. May 4

Table I

Scale	Time
41.60	1:35
41.80	1:37
42.00	1:40
42.10	1:43
42.20	1:49
42.30	1:55
42.40	2:04
42.47	2:12
42.55	2:23
42.70	2:38
42.77	2:50
42.85	3:08
42.90	3:35
43.00	5:06
43.02	6:15
✓43.10	8:30
43.20	3:00 P.M. May 5
43.28	9:00 A.M. May 6

✓apparent setting time

Table II

Time (min.)	$\frac{x}{a-x}$
18	1.4
30	2.2
60	4.0
98	6.8
176	11.5
340	22.0

Scale limits by extrapolation:

40.02-43.22 ∴ .0552 moles per 1.% a = 3.20

Sample calculation:

at t = 60 min., x = 2.54
a-x = .66

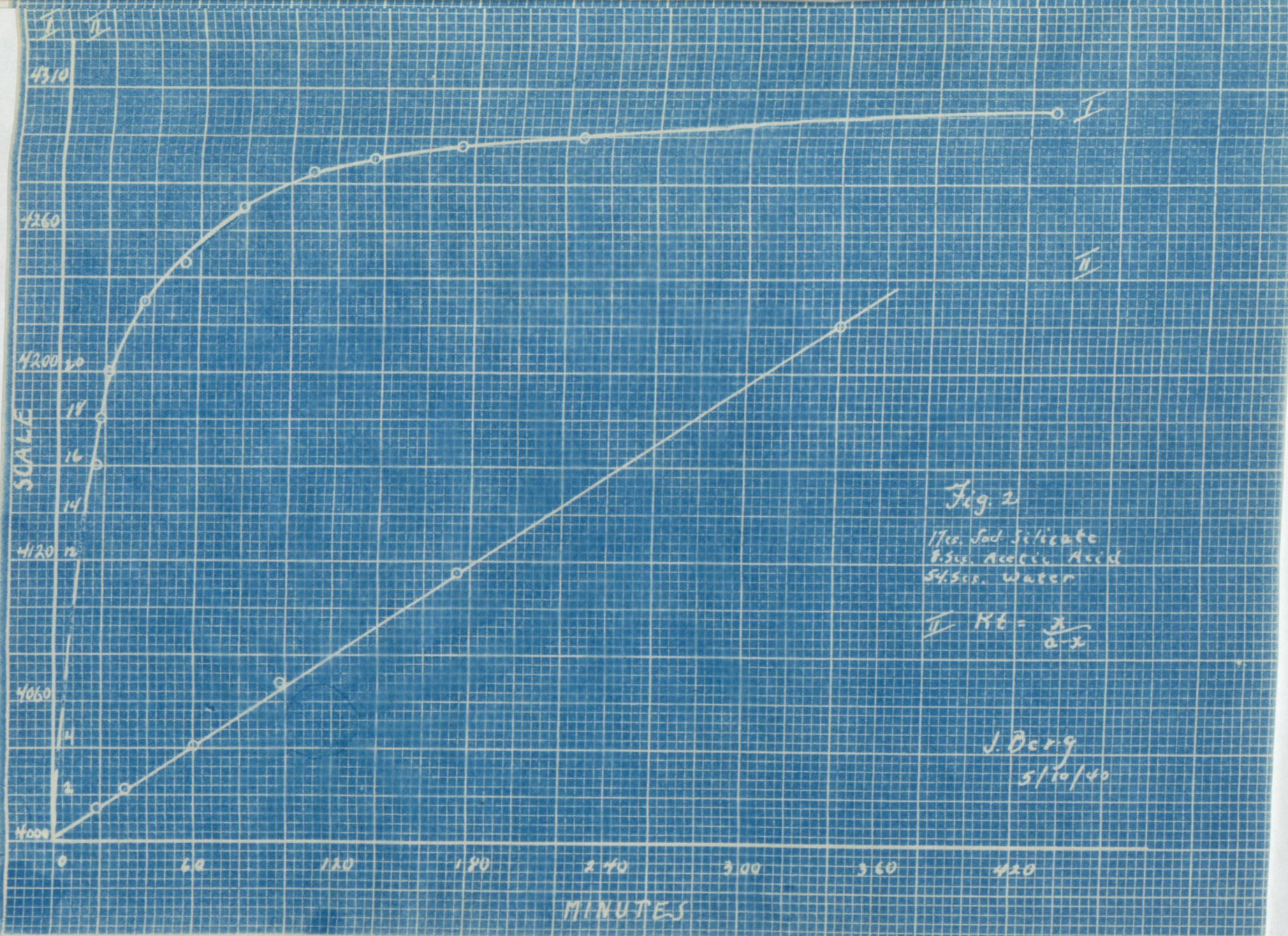
so $\frac{x}{a-x} = \frac{2.54}{.66} = 4$

Specific reaction rate $k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$

$k = \frac{1}{60 \text{ min.}} \cdot \frac{\frac{2.54}{3.20}\ (.0552 \text{ mols per liter})}{.0552 \text{ mols/l.}\left(.0552 \text{ mols/l.} - \frac{2.54}{3.20}(.0552 \text{ mols/l.})\right)}$

$k = .0666 \ \frac{\text{liters}}{\text{minutes moles}}$

Volume change = .0223 c.c.
% change = .054%


I
II
4310
4260
4200
4120
4060
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SCALE
20
18
16
14
12
10
8
0
20
120
180
240
300
360
420
MINUTES
I
II
Fig. 2
11cc. Sod. Silicate
1.5cc. Acetic Acid
54.5cc. Water
II Kt = x/a-x
J. Berg
5/10/40

Figure 3

17 c.c. Sodium Silicate 1.6268 N
7.1 c.c. Acetic Acid 5.1750 N
55.9 c.c. Water
Temperature 25° C ± .01°

Dilatometer 3 - Radius .43 mm.
Scale, 1 unit = 1.05 cm.
Volume 41.30 c.c.
Mixing time - 2:48 P.M. May 6

Table I

Scale	Time
41.20	2:58
41.40	3:00
41.60	3:04
41.70	3:07
41.80	3:10
41.90	3:14
42.00	3:21
42.10	3:30
42.28	4:00
42.30	4:11
42.34	4:37
42.37	5:30
42.40	5:55
✓	6:10

✓ Apparent setting time

Table II

Time (min.)	$\frac{x}{a-x}$
12	1.8
36	6.0
176	13.6
140	25.7

Scale limits by extrapolation

39.28–42.50 or .0552 mols per l. γ a = 3.22

Sample calculation:

at t = 36, x = 42.03–39.28 = 2.75
a–x = .47

so $\frac{x}{a-x} = \frac{2.75}{.47} = 6$

Specific reaction rate $k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$

$\frac{2.75}{3.22}$ (.0552 mols per liter)

$k = \frac{1}{36 \text{ min.}} \cdot \frac{}{.0552 \text{ m. pl.} \left(.0552 \text{ m pl.} - \frac{2.75}{3.22}(.0552 \text{ m pl.})\right)}$

$k = .166 \frac{\text{liters}}{\text{min. moles}}$

Volume change = .0225 c.c.
% change = .054%

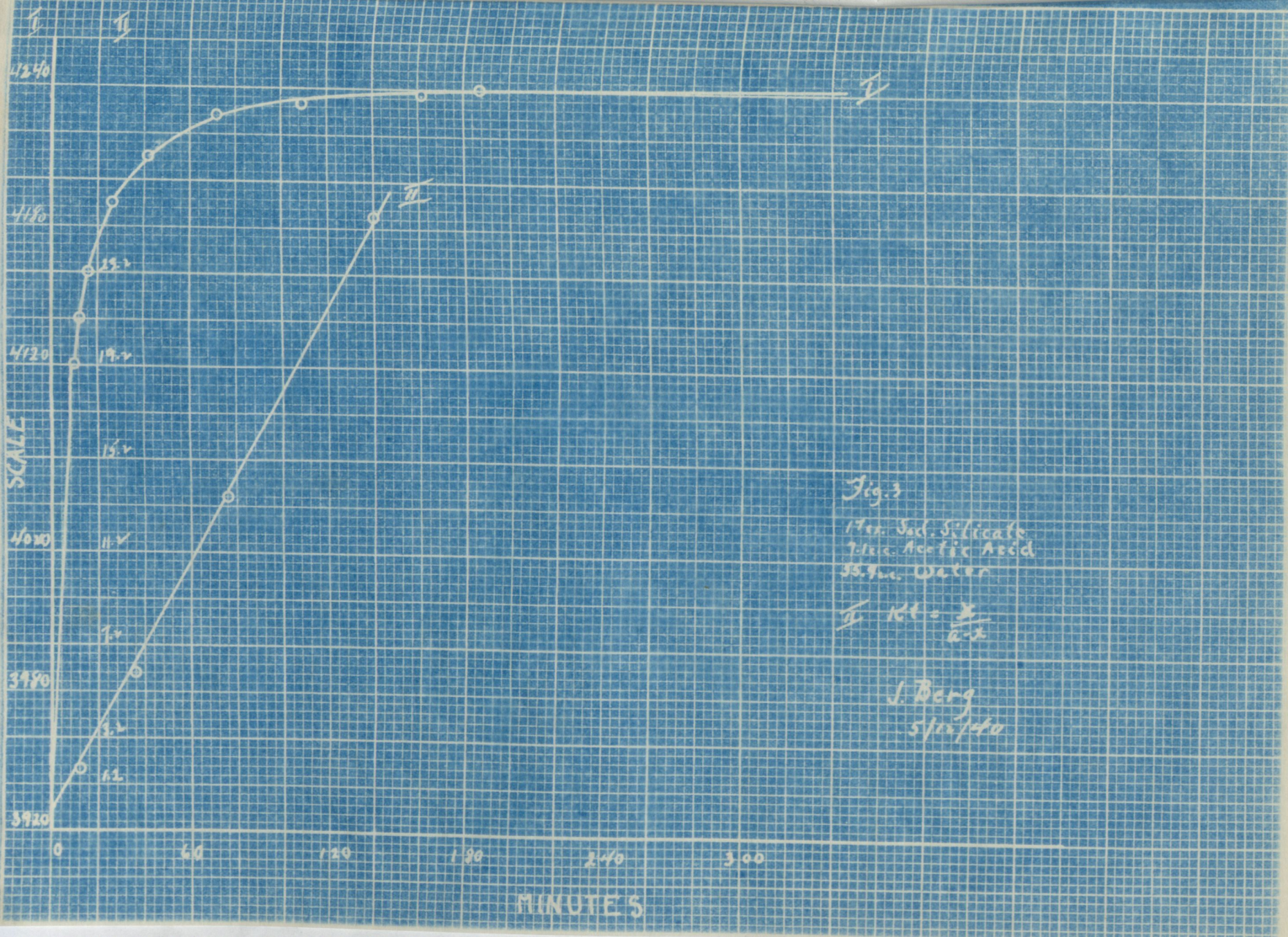


Fig. 3

17 cc. Sod. Silicate
3 cc. Acetic Acid
35 cc. Water

$K = \frac{x}{a-x}$

J. Berg
5/12/40

Figure 4

17 c.c. Sodium Silicate 1.6268 N
7.3 c.c. Acetic Acid 5.1750 N
55.7 c.c. Water
Temperature 25° C. ± .01°-.03°

Dilatometer 3 - Radius .43 m.m.
Scale, 1 unit = 1.05 cm.
Volume - 43.70 c.c.
Mixing time - 2:02 P.M. Mar. 25

Table I

Scale	Time	Temperature
42.35	2:22	25.03
42.40	2:25	25.03
42.53	2:33	25.01
42.60	2:38	25.00
42.65	2:44	25.00
42.70	2:50	25.02
42.90	3:00	25.00
42.92	3:20	25.02
43.10	3:35	25.00
43.15	3:40	25.02
43.22	4:06	25.00
43.35	4:32	25.00
43.36	4:45	25.02
43.42	5:12	25.02
✓ 43.45	5:25	25.02
44.00	10:25 A.M. Mar. 27	
44.25	9:00 A.M. Mar. 28	
44.55	6:00 P.M. Mar. 29	

✓ Apparent setting time

Table II

Time (min.)	$\frac{x}{a-x}$
24	2.0
36	2.7
60	4.5
112	9.7
180	15.9

Scale limits by extrapolation

4015-4350 ∴ .0552 mols per l. ∝ a = 3.35

Sample calculation:

at t = 24 min., x = 4240-4015 = 2.25
a-x = 1.10

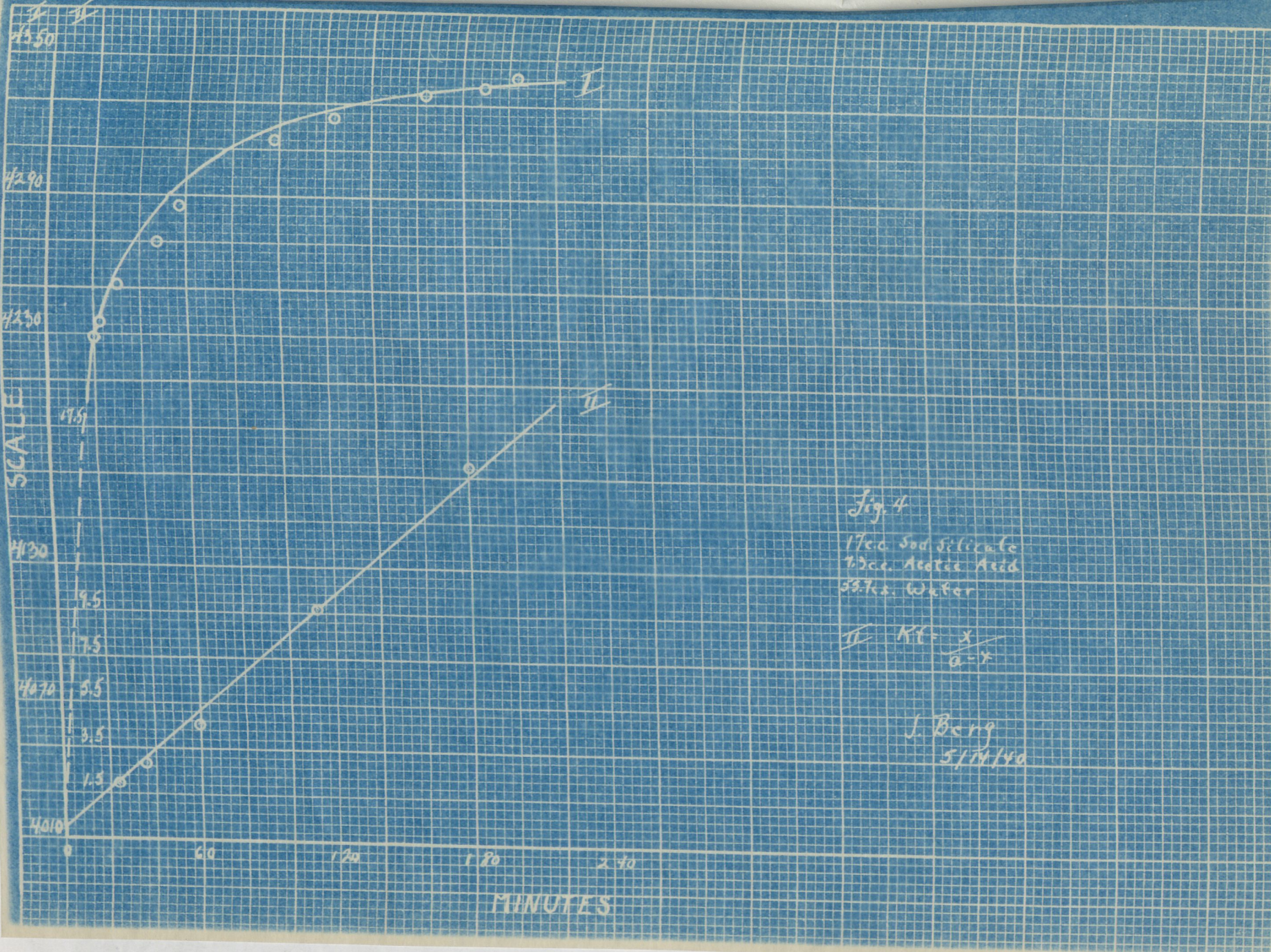
so $\frac{x}{a-x} = 2$

Specific reaction rate $k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$

$$k = \frac{1}{24 \text{ min.}} \cdot \frac{\frac{2.25}{3.35}\ (.0552 \text{ mols per liter})}{.0552 \text{ m.p.l.} \left(.0552 \text{ m.p.l.} - \frac{2.25}{3.35}(.0552 \text{ m.p.l.})\right)}$$

$$k = .083 \ \frac{\text{liters}}{\text{min. moles}}$$

Volume change = .0234 c.c.
% change = .053%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1560
1620
1680
1740
1800
1860
1920
1980
2040
2100
2160
2220
2280
2340
2400

DATA

A

17 c.c. Sodium Silicate
11.5 c.c. Acetic Acid
51.5 c.c. Water
Dilatometer 3
Volume 42.85
Mixing time 1:44 P.M. April 30
Temperature 25° C. ± .01°

Scale	Time
43.60	1:56
43.80	1:58
44.00	2:01
44.10	2:03
44.20	2:05
44.30	2:07
44.40	2:10
44.50	2:14
44.65	2:18
44.70	2:21
44.90	2:35
45.00	2:43
45.20	3:07
45.30	3:29
45.45	4:27
45.52	5:06
45.68	8:30
✓45.78	10:25
45.86	8:00 A.M. May 1
46.12	11:00 A.M. May 2
46.28	11:00 A.M. May 3

✓ Apparent time of set

B

17 c.c. Sodium Silicate
11.5 c.c. Acetic Acid
51.5 c.c. Water
Volume 42 c.c.
Mixing time 2:23 P.M. April 15
Dilatometer 6 - Radius .43 m.m.
Scale, 1 unit = 1.1

Scale (reversed)	Time
19.10	2:47
18.95	2:50
18.85	2:54
18.80	2:56
18.53	3:07
18.49	3:12
18.41	3:17
18.35	3:24
18.30	3:33
18.20	3:40
18.15	3:44
18.10	3:49
18.05	4:02
17.95	4:23
17.87	4:40
17.80	4:55
17.77	5:19
17.75	5:32
17.41	9:20
✓17.37	11:00 P.M.